

The University of Chicago

THE VARIATION OF THE HEATS OF
DILUTION OF HYDROCHLORIC
ACID SOLUTIONS WITH
TEMPERATURE

A DISSERTATION SUBMITTED TO THE FACULTY
OF THE DIVISION OF THE PHYSICAL SCIENCES
IN CANDIDACY FOR THE DEGREE OF DOCTOR
OF PHILOSOPHY

DEPARTMENT OF CHEMISTRY

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JAMES RODERICK MacDONALD

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Introduction

The theory of Debye and Hückel, first published in 1923, introduced a method for calculating the limiting heats of dilution of strong electrolytes. Before their theoretical work, five men had contributed to the measurements of heats of dilution of hydrochloric acid.¹ The results obtained by the latter, however, were not consistent and therefore were important only in that they laid the foundation for future work. These heats of dilution were not sufficiently accurate to test the theory of Debye and Hückel, nor were they accurate enough to be used in the calculation of activity coefficients from freezing point data. Lewis and Randall² pointed out the extreme necessity for accurate results on heats of dilution before an accurate determination of activity coefficients from freezing point data could be made. The Debye-Hückel theory, together with the work of Lewis and Randall, encouraged more precise measurements of the properties of strong electrolytes and led to increased activity in this field.³

The purpose of the work described in this paper is to furnish a sufficiently accurate and extensive determination of

¹ Cf. Buck, Ph.D. Dissertation, University of Chicago (1935) for a discussion of the work of Berthelot, Steinwehr, Muller, and Richards and Rowe.

² Lewis and Randall, "Thermodynamics," McGraw-Hill Book Company, New York (1923).

³ Cf. Buck, *op. cit.*, for a discussion of the work of Wrensky and Bawaritzky, Richards, Mair and Hall, and Rossini.

the heats of dilution of hydrochloric acid for calculating the activity coefficients of hydrochloric acid from freezing point data.

Apparatus

The apparatus used had been developed by Dr. T. F. Young and his co-workers⁴ in the course of their investigations of heats of dilution. The essential parts of the apparatus are described in the following paragraphs. A more detailed description of most of these parts may be found in the theses of Vogel, Groenier, Machin, and Buck.

The calorimeter used was a silvered pyrex glass Dewar which had a capacity of one and one-half liters. The dilution vessel was a tantalum can having a capacity of seventy-five cubic centimeters. It was supported in the calorimeter by two glass rods which were inserted through four tantalum loops - two on each side of the can. The upper ends of the glass rods projected through two brass chimneys on the top of the calorimeter. Rubber tubing placed over each chimney and its glass rod held the two firmly together. The can was tested by substituting distilled water for the acid solution, and no heat effect could be detected in the results. It was found that the contents of the can required thirty to forty seconds to become thoroughly mixed with the surrounding liquid in a glass vessel similar in size and shape to the calorimeter Dewar.

The stirrer also was made of tantalum and was cemented into a glass tube in order to minimize heat leakage. When the stirrer was in position in the calorimeter, the upper propeller was approximately two centimeters below the surface of the liquid and two

⁴Cf. Ph.D. Dissertations, University of Chicago, by Vogel (1930), Groenier (1931), Machin (1932), and Buck (1935).

centimeters above the top of the dilution vessel. Later, the upper propeller was lowered to five centimeters below the surface of the liquid. A small synchronous motor rotated the stirrer at 450 revolutions per minute.

The temperature change inside the calorimeter was measured by a twenty-four junction copper-constantan thermel.⁵ The copper wire was No. 32, and the constantan No. 24 of Brown and Sharpe gauge. One end of the thermel was inserted into the calorimeter through a chimney on top of the calorimeter. The other end extended through a split stopper, into a small-necked silvered Dewar. In this way the reference end of the thermel was kept at a constant temperature during each experiment.

The resistance unit of the heater was encased in a platinum sheath from which it was insulated by sheets of mica. A platinum iridium conduit contained the electrical lead wires and supported the heater in the calorimeter.

The thermostat consisted of a tank which measured 76 x 76 x 61 centimeters. Because of the occurrence of rapid temperature changes in the room, a space above the thermostat tank, 67 centimeters high, was enclosed by pieces of celotex which were removable on three sides. The thermostat was filled with approximately seventy-five liters of water, called the bath. The bath was maintained, for at least six hours, at a temperature which varied within .001 degree by a mercury-filled glass tube which controlled a five-hundred, and later a two-hundred-and-fifty watt bulb by means of a relay. In previous experiments the tube holding the mercury had been closed at one end with a stop-cock. Temperature variations as large as 0.3 of one degree were found to accompany atmospheric pressure changes. It was concluded that

⁵Machin, op. cit., pp. 6-7.

these changes were caused by air in the tube. Therefore, the mercury was introduced into the tube at a pressure of 2×10^{-5} centimeters of mercury, and one end of the tube was sealed. As a result, observations over a period of one week showed that the variation in the temperature of the thermostat was reduced to 0.03 degree.

The double potentiometer used for measuring the electromotive force in these experiments was designed by White and was built by Leeds and Northrup Company. The galvanometer was a Type H S made by Leeds and Northrup. It was mounted at a distance of four meters from the scale. A brass plate, $1/8$ inch thick, 1 inch wide, and 3 inches long, was mounted on the face of the galvanometer to support a small mirror. The plate had an opening of $3/4$ inch by $1/2$ inch, through which the galvanometer mirror could be seen. Three screws inserted in the plate served as adjustable legs and made it possible to regulate the position of the external mirror so that an electrically operated clock could be seen through the telescope. The clock was placed in such a position that both it and the reflection of the galvanometer scale would be brought into focus by the same adjustment of the telescope. Because it was more convenient to read both clocks as the second hands crossed sixty, the small electric clock, which was read through the telescope, was set one-half minute ahead of the control clock.

The heating circuit which had been used in previous work was rebuilt before the present experiments were begun. The bakelite strips, which formerly supported both the heater and the potentiometer leads, were cut so as to separate the two types of leads. One portion of each strip was then moved along its supporting and grounded wires. The current for the heating

circuit was supplied by a fifty-volt bank of storage batteries. To allow the current from the batteries to become steady, it was passed through the auxiliary resistance for at least one hour before each experiment. If the batteries had just been charged, this period was increased to four hours. To insure an exact period of heating, a clock closed and opened the heating circuit by means of a switch system.

Two pyrex weight burettes were used in the determination of the quantity of solution and of water used in each experiment. The large burette, which had been cooled after it was weighed, was wrapped in a paper towel to prevent the moisture which condensed on the burette from diluting the solution. The weight burettes were treated in this manner before each weighing to insure a constant error. All weighings were corrected for buoyancy.

The cooling of the thermostat was accomplished by iced brine at 0° C. and iced water at $12\frac{1}{2}^{\circ}$ C. The brine or water was circulated from a reservoir at the side of the thermostat through a copper cooling coil in the thermostat and returned to the top of the reservoir. When experiments were made at 0° C., it was necessary to use 3 per cent ethyl alcohol in the bath to prevent the insulation of the coil by the formation of ice upon it. A $\frac{3}{8}$ inch gear pump, model EFRC manufactured by Viking Pump Company, was used in circulating the ice-water or brine. The brine was drawn through a double screen from the reservoir filled with a mixture of ice and salt. When the experiments were made at $12\frac{1}{2}^{\circ}$ C., the ice-water was drawn from the reservoir through orifices in the pipe.

The reservoir was a steel barrel having a capacity of approximately fifty gallons. It was insulated with excelsior and

was surrounded by a box to hold the insulation in place. About 200 pounds of ice and 15 pounds of rock salt were required every twenty-four hours in order to maintain the bath at 0° C., and 125 pounds of ice were used each day to maintain the bath at $12\frac{1}{2}^{\circ}$ C.

Materials

The solutions for the dilution experiments, with the exception of the 3.9439 molal and 4.8834 molal solutions, were made from distilled hydrochloric acid (Baker and Adamson's C.P. Reagent Quality Hydrochloric Acid), obtained from the still described by Buck.⁶ The 3.9439 and 4.8834 molal solutions were made up directly from the C.P. Acid. All of the solutions were analyzed by silver-chloride precipitation - as described by Hartsuch,⁷ except that distilled water was substituted for conductivity water. The solutions were stored in five-liter pyrex flasks stoppered with corks (which had been treated with hot paraffin). During the withdrawal of the solutions, the flasks were stoppered with rubber treated with molten vaseline. A siphon inserted through a hole in the rubber stopper was used to draw out the solutions.

Procedure

The solutions were weighed in the large burette, and the water in the smaller one. The large burette filled with the solution was suspended in the ice or brine of the reservoir for an hour or more when the experiments were made at $12\frac{1}{2}^{\circ}$ C., and for two hours or more when the determinations were being made at 0° C. The solution was transferred into the calorimeter, and the

⁶Buck, op. cit., p. 13.

⁷Hartsuch, Ph.D. Dissertation, University of Chicago (1935).

water was sealed in the dilution vessel by means of vaseline. The apparatus was assembled as rapidly as possible to prevent absorption of heat and was then placed in the thermostat. For lower concentrations of the solutions, the thermel was inserted in the chimney immediately after the calorimeter was put in place. For the concentrated solutions, the thermel was inserted through the chimney on the top of the calorimeter and wired into a rubber tube on the chimney; vaseline was applied at the bottom of the chimney to prevent the fumes of hydrochloric acid from entering it.

The stirrer was started, the difference in temperature between the calorimeter and the bath was observed, and an estimate of the temperature was made. Next, the heater was turned on and the calorimeter was brought to a temperature a little below that desired.

After approximately three liters of liquid had been pumped through it, the small-necked Dewar was placed on the end of the thermel. The temperature of the calorimeter was raised at short intervals by means of the heater until it was decreasing at a rate of less than 0.03 microvolt per minute. The temperature variation was maintained within this limit for at least one hour before the experiment was started.

When the apparatus was ready for a dilution experiment, the temperature of the thermostat was recorded, and the sensitivity of the thermel determined. The thermel readings were then recorded for about ten minutes, the dilution vessel was opened on the half minute (on the small clock), and the thermel readings continued for eleven minutes more. The current was passed through the heater for a three-minute period and again the thermel readings were taken for eleven minutes. This last procedure was

TABLE I

0° C.

m_1	$\sqrt{m_1}$	$\sqrt{m_2}$	t 0.01°	t in uv.	Heat capacity calorimeter and contents			ρ_H	P_t	P
					15° calories per uv.					
					1	2	Mean			
0.3707	0.60884	0.58150	0.08	2.11	.9749	.9743	.9746	7.286	266.6	267.0
0.3707	0.60884	0.57955	0.04	2.29	.9190	.9181	.9185	7.945	271.3	271.5
0.5605	0.74375	0.71540	0.09	4.10	.9787	.9770	.9778	9.293	278.6	279.2
0.5605	0.74875	0.71706	0.12	3.88	.9840	.9833	.9836	8.791	277.4	278.2
0.7958	0.89210	0.85276	0.04	7.27	.9682		.9682	11.435	290.7	291.0
0.7958	0.89210	0.85221	0.09	7.29	.9576	.9581	.9579	11.524	288.9	289.6
1.0415	1.02054	0.97345	0.04	12.23	.9102	.9103	.9103	14.641	310.9	311.2
1.0415	1.02054	0.97490	0.04	11.86	.9539	.9536	.9537	14.231	311.8	312.1
1.6411	1.28105	1.22442	0.10	28.61	.9289	.9296	.9292	21.482	379.3	380.1
1.6411	1.28105	1.22296	0.11	29.41	.9407		.9407	22.143	381.2	382.1
1.7264	1.31393	1.25465	0.05	32.86	.9368	.9374	.9371	23.320	393.4	393.7
1.7264	1.31393	1.25561	0.03	32.43	.9247	.9247	.9247	23.028	394.9	395.2
2.7611	1.66166	1.58509	0.12	91.95	.8927	.8921	.8924	40.142	524.3	525.4
2.7611	1.66166	1.58588	0.10	91.18	.8966	.8967	.8967	39.673	523.5	524.4
3.9439	1.98593	1.89162	0.10	210.84	.8594	.8591	.8593	63.761	675.3	676.2
3.9439	1.98593	1.88884	0.09	217.66	.8332	.8342	.8337	65.490	674.5	675.3
4.8834	2.20934	2.10001	0.03	353.18	.8243	.8231	.8237	85.195	782.5	783.4
4.8834	2.20934	2.10272	0.07	351.94	.8270	.8264	.8267	83.844	782.0	782.8

TABLE II

12 1/2° C.

m_1	$\sqrt{m_1}$	$\sqrt{m_2}$	t 0.01°	t in uv.	Heat capacity calorimeter and contents 150 calories per uv.			ϕH	P_{t^0}	P
					1	2	Mean			
0.3707	0.60884	0.58181	12.54	2.70	.9630	.9622	.9626	9.000	333.1	333.9
0.3707	0.60884	0.58185	12.61	2.68	.9590	.9590	.9590	9.050	333.4	334.9
0.5605	0.74867	0.71598	12.45	5.15	.9671	.9670	.9671	11.386	348.3	348.1
0.5605	0.74867	0.71621	12.46	5.16	.9623	.9612	.9618	11.366	350.0	349.8
0.79584	0.89210	0.85244	12.42	9.52	.9405	.9499	.9499	14.755	372.0	371.6
0.79584	0.89210	0.85197	12.42	9.69	.9405	.9392	.9399	14.985	373.4	373.0
1.0415	1.02054	0.97446	12.44	15.42	.9479	.9472	.9475	18.225	395.5	395.2
1.0415	1.02054	0.97452	12.43	15.43	.9414	.9412	.9413	18.143	394.2	393.8
1.6411	1.28105	1.22393	12.44	36.57	.9159	.9171	.9165	26.959	471.9	471.5
1.6411	1.28105	1.22341	12.43	37.06	.9187	.9177	.9182	27.222	472.3	471.8
1.7264	1.31393	1.25514	12.61	40.38	.9245	.9252	.9248	28.431	483.7	484.4
1.7264	1.31393	1.25531	12.49	41.29	.9050	.9050	.9050	28.456	485.5	485.4
2.76112	1.66166	1.58241	12.52	115.22	.8527	.8524	.8525	48.606	620.7	620.7
2.7611	1.66166	1.58335	12.48	113.82	.8590	.8585	.8587	49.284	621.8	621.7
3.9439	1.98593	1.89026	12.47	250.92	.8255	.8255	.8255	73.740	770.8	770.6
3.9439	1.98593	1.89260	12.49	245.21	.8435	.8429	.8432	71.893	770.4	770.3
4.8834	2.20984	2.10509	12.48	398.80	.8222	.8215	.8219	93.867	895.7	895.5
4.8834	2.20984	2.10398	12.47	403.23	.8159	.8160	.8160	94.658	893.7	893.5

TABLE III

25° C.

m_1	$\bar{m}_1$	$\bar{m}_2$	$t_{0.01}$	t in uv.	Heat capacity calorimeter and contents 15° calories per uv.			ϕ_H	T_0	$\bar{P}$
					1	2	Mean			
0.3707	0.60884	0.58194	24.98	3.14	.9455	.9292	.9292	10.083	374.9	375.0
0.3707	0.60884	0.58176	25.20	3.11		.9453	.9454	10.117	373.6	373.1
0.5605	0.74867	0.71355	24.93	6.55	.3798	.8793	.8795	14.047	400.0	400.2
0.5605	0.74867	0.71318	24.93	6.52	.8592	.8586	.8589	13.982	394.0	394.2
0.7743	0.87996	0.84063	24.98	10.91	.9207	.9208	.9207	16.822	428.1	428.2
0.7743	0.87996	0.84161	24.98	10.70	.9310	.9320	.9315	16.458	429.1	429.2
1.0415	1.02054	0.97318	24.93	19.04	.8623	.8626	.8624	21.735	458.9	459.3
1.6411	1.28105	1.21869	24.94	46.67	.8311	.8305	.8308	33.606	538.9	539.1
1.6411	1.28105	1.21972	24.95	46.82	.8549	.8541	.8545	32.981	537.8	538.1
1.7264	1.31393	1.25533	25.02	47.93	.8938	.8938	.8938	32.725	558.5	558.4
1.7264	1.31393	1.25384	24.98	48.93	.8897	.8910	.8904	33.441	556.6	556.8
3.9439	1.98593	1.87922	24.95	309.49	.7229	.7236	.7232	90.647	849.5	849.8
3.9439	1.98593	1.87471	24.95	319.87	.7010	.7016	.7013	94.200	847.0	847.4
4.8334	2.20924	2.08636	24.92	512.18	.6793	.6794	.6794	120.124	972.8	973.2
4.8334	2.20924	2.08738	24.94	508.55	.6962	.6956	.6959	119.475	975.6	975.9

repeated for a check of the heat-capacity data.

In the middle of the heating period,⁸ the current was measured on the B dials of the potentiometer. Later, the measurements necessary for the determination of the resistance of the heater was made, and the sensitivity of the galvanometer in the P and Q circuits was determined.

Calculations and Results

The method used in the calculation of $\bar{F}$ has been described by Machin.⁹ The results of the calculation of the data for 0° C., 12 1/2° C., and 25° C. for hydrochloric acid are shown in Tables I, II, and III, respectively. The results are shown graphically on the following chart, with $\bar{F}$ for each molality plotted as the ordinates and the values of $m^{\frac{1}{2}}$ as the abscissae. In the plotting of $m^{\frac{1}{2}}$, the values for both $m^{\frac{1}{2}}_1$ and $m^{\frac{1}{2}}_2$ were plotted and a chord drawn between each pair. The curves of the chart were drawn through the true point of each chord. It is noted that the curves for the three temperatures tend to converge as the molality decreases and this tendency is much more noticeable as the molality becomes less than one. This tendency to converge is shown more clearly by plotting the difference between the chords at 0° and 12 1/2°, and 12 1/2° and 25°, as pictured at the bottom of the chart.

The author's indebtedness to Dr. T. F. Young for his valuable criticism, assistance, and suggestions during the course of this study is herewith gratefully acknowledged.

⁸A complete statement of the mechanics of the heating period may be found in Buck, op. cit., pp. 16-17.

⁹Machin, op. cit.

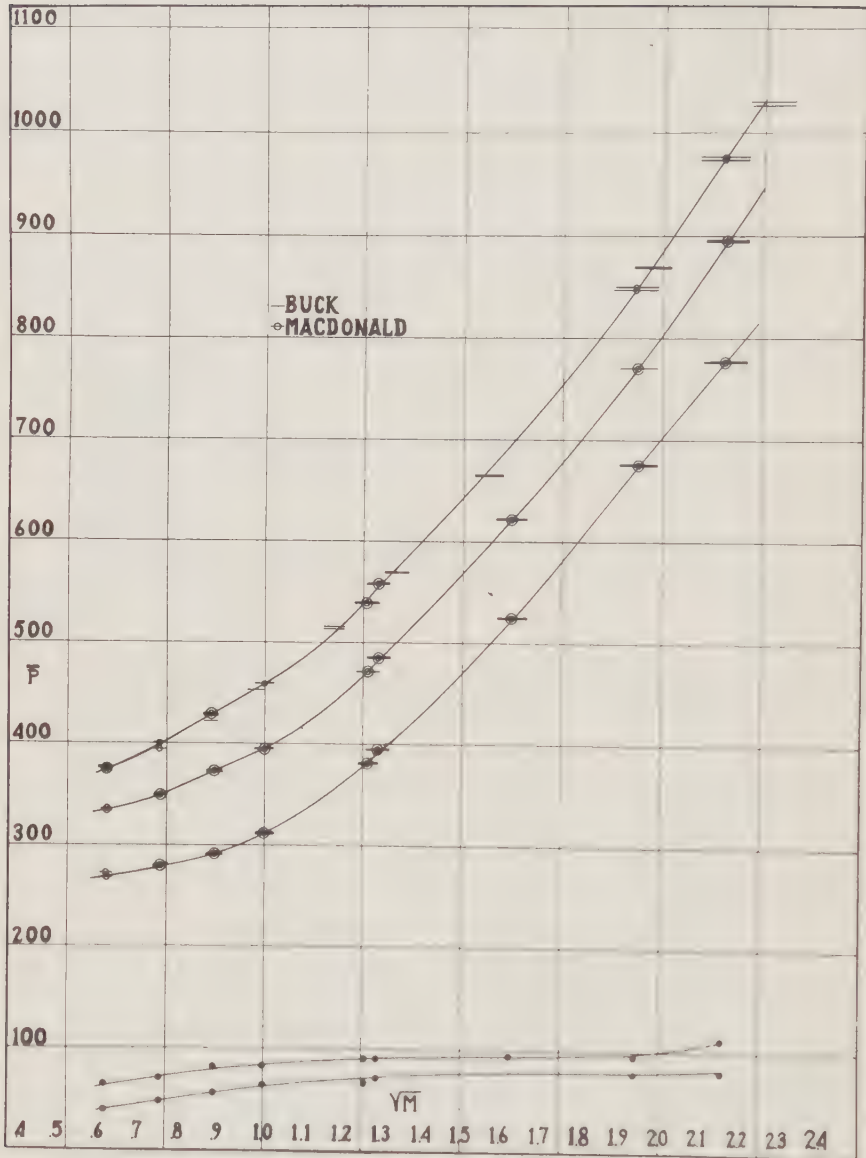


Fig. 1.

